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(54) **Organic electrolytic solution cell**

Zelle mit organischer Elektrolytlösung

Pile à solution électrolytique organique

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Description

[0001] The present invention relates to an organic electrolytic solution cell which has good shelf stability.

[0002] Organic electrolytic solution cells, a typical example of which is a manganese dioxide-lithium cell, are increasingly used, since they generate a high voltage and have a high energy density.

[0003] A perchlorate base electrolyte such as $LiClO_4$ is generally used as an electrolyte to be contained in an electrolytic solution used in such organic electrolytic solution cell. Recently, in view of safety of the cells, it is undesirable to use dangerous materials such $LiClO_4$ in the cells.

[0004] Apart from $LiClO_4$, boron lithium salts such as $LiBF_4$ or $LiB(C_6H_5)_4$ are used as the lithium salt electrolytes.

[0005] However, when such boron lithium salt is used as the electrolyte, the electrolytic solution tends to be discolored or polymerizes some kinds of media of the electrolytic solution during storage. When such electrolytic solution is used in the cell, a shelf stability of the cell is shortened.

[0006] One object of the present invention is to provide an organic electrolytic solution cell in which the electrolyte is not discolored or does not polymerize a medium.

[0007] Another object of the present invention is to provide an organic electrolytic solution cell which has a long shelf stability.

[0008] According to a first aspect of the present invention, there is provided an organic electrolytic solution cell having a cell voltage exceeding 3 V comprising a positive electrode, a negative electrode which is made of an alkali metal or a compound comprising an alkali metal, and an organic electrolytic solution which contains, as an electrolyte, an organic salt comprising an anion having an atom selected from the elements of the IIIb, IVb and Vb groups of the Periodic Table as an anion center in which an electron attractive group is bonded to said atom, and a counter cation in a molar ratio of said counter cation to said anion center atom of larger than 1.

[0009] According to a second aspect of the present invention, there is provided an organic electrolytic solution cell comprising a positive electrode, a negative electrode which is made of an alkali metal or a compound comprising an alkali metal, and an organic metal salt comprising an atom selected from the group consisting of the elements of IIIb to Vb groups of the Periodic Table which forms an anion center and an electron attractive organic group bonded to said atom through an oxygen atom.

[0010] According to a third aspect of the present invention, there is provided an organic electrolytic solution cell comprising a positive electrode, a negative electrode, which is made of an alkali metal or a compound comprising an alkali metal, and an organic electrolytic solution which contains, as an electrolyte, an organic metal salt comprising an atom which forms an anion center and a counter cation in a molar ratio of said counter cation to said anion center atom of larger than 1.

[0011] The Figure shows a cross sectional view of an organic electrolytic solution cell.

[0012] One of the characteristics of the present invention is that the above specific organic metal salt is used as an electrolyte of the electrolytic solution cell.

[0013] The atom of the IIIb, IVb and Vb groups forming the anion center, for example, boron (B), nitrogen (N), phosphorus (P), gallium (Ga), aluminium (Al), silicon (Si) and the like, has a smaller electro-negativity than the atoms of the VIb group such as oxygen (O) and sulfur (S). In the case where the electrolyte comprises the atoms of the IIIb to Vb groups which forms the anion center, when the cell voltage exceeds 3 V, the electrons are easily liberated because of the small electronegativity so that the anion is oxidized, and then the shelf stability of the cell tends to deteriorate.

[0014] To prevent the oxidation of the anion as described above, it may be contemplated that the electron attractive group is bonded to the atom of the IIIb to Vb groups which forms the anion center to stabilize the atom as the anion center. An example of a compound which is stabilized in this way is $LiBF_4$. Though, $LiBF_4$ has stability to some extend, its stability is not satisfactory as seen from Comparative Example 2 described later.

[0015] According to the first aspect of the present invention to further stabilize the organic metal salt as the electrolyte, an oxygen atom is bonded to the atom of the IIIb to Vb groups which forms the anion center, and the electron attractive group is bonded to the oxygen atom.

[0016] While it may be possible to form an organic metal salt from an atom having a high electronegativity such as the VIb group atoms, for example, oxygen and sulfur, the formed organic metal salt cannot function as an electrolyte since only one electron attractive group is bonded to the oxygen atom so that the salt is hardly dissolved in a solvent.

[0017] The reason why the electron attractive group is bonded to the anion center atom through the oxygen atom is that the oxygen atom has the high electronegativity so that it can decrease an electron density on the atom forming the anion center and then stabilize the atom forming the anion center against the oxidation, and that the oxygen has two valencies so that it can bond the electron attractive organic group in a state of a low steric hindrance.

[0018] The electron attractive organic group attracts the electron from the atom forming the anion center through the oxygen atom to decrease an electron density of the atom forming the anion center, whereby it becomes difficult to withdraw the electron from the anion center and then the oxidation of the anion is prevented.

[0019] Examples of the electron attractive organic group are a carbonyl group, a sulfonyl group, an amino group, a

cyano group, a halogenated alkyl group having 1 to 20 carbon atoms, and the like. Among them, the carbonyl group is preferred, since the organic metal salt having the carbonyl group can be synthesized easily.

[0020] Examples of metals which form the salts with the above electron attractive organic group are alkali metals such as lithium, sodium or potassium, alkaline earth metals such as magnesium or calcium, and the like. Among them, lithium is preferred.

[0021] Preferably, a molar amount of the metal forming the counter ion is larger than that of the atom forming the anion center. The reason for this will be explained later.

[0022] Specific examples of the organic metal salt is a compound of the formula:

$$LiBXX'$$

or

$$LiB(=O)X$$

wherein X and X' are the same or different and each an electron attractive organic group having an oxygen atom which bonds to the boron atom and, for example, a group of the formula: -O-C(=O)-C_6H_3(R)-O- or a group of the formula: -O-C(=O)-R'-O- in which R is a hydrogen atom or an alkyl group having 1 to 20 carbon atoms and R' is an alkylene group having 1 to 20 carbon atoms;

$$LiB(Y_1)(Y_2)(Y_3)(Y_4)$$

wherein Y_1, Y_2, Y_3 and Y_4 are the same or different and each a group of the formula: -O-C(=O)-R, a group of the formula: -O-R or a group of the formula: -C(=O)-O-R provided that at least one of Y_1, Y_2, Y_3 and Y_4 is a group of the formula: -O-C(=O)-R;

LiN[-OC(=O)CF_3][-C(=O)CF_3], and the like. Among them, lithium boron disalicylate [LiB(-O-C(=O)-C_6H_4-O-)$_2$] is particularly preferred.

[0023] LiN[-OC(=O)CF_3][-C(=O)CF_3] may be prepared by neutralizing NH[-OC(=O)CF_3][-C(=O)CF_3] with a basic lithium salt. Lithium boron disalicylate may be prepared by the method described in J. Inorg. Nucl. Chem., 40, (1978) 987 or by mixing boric acid, salicylic acid and a basic lithium salt in a determined molar ratio, reacting them in an organic solvent by heating while removing water and removing the solvent.

[0024] Other examples of the organic metal salt which can be used as the electrolyte in the present invention are $LiB(OSO_2Rf)_4$, $LiC(OSO_2R_f)_3$, $LiN(OSO_2R_f)_2$ (wherein R_f is a fluoroalkyl group having 1 to 20 carbon atoms), and the like.

[0025] As the atom which forms the anion center, any one of the elements of the IIIb to Vb groups of the Periodic Table, such as a boron atom (B), nitrogen (N), a phosphorus atom (P), a gallium atom (Ga), an aluminum atom (Al), a silicon atom (Si), and the like can be used. In view of the valency, the atoms of the IIIb and IVb groups, in particular the atoms of the IIIb group are preferred. In view of a molecular weight of the organic metal salt, the atom having an atomic weight of 70 or less, preferably 30 or less, more preferably 15 or less is desirable.

[0026] In view of these factors, the boron atom is particularly preferred, since it has the atomic weight of 10.8 and it provides four bonds which is more than the bonds provided by the oxygen or nitrogen atom when it forms the anion center, so that it can bond with more electron attractive organic groups through the oxygen atom than other atoms which form the anion center.

[0027] In the second aspect of the present invention, a molar ratio of the metal forming the counter cation to the atom forming the anion center is larger than 1, whereby the shelf stability of the cell is improved.

[0028] Preferably, this molar ratio is at least 1.001, more preferably at least 1.005, most preferably at least 1.02.

[0029] When this molar ratio exceeds 1.05, the cell characteristics may start to decrease. Then, the molar ratio is preferably 1.05 or less.

[0030] The reason why the shelf stability of the cell can be improved when the above molar ratio is larger than 1 may by that the organic metal salt used according to the present invention and a hardly soluble salt such as Li_2CO_3 may form a double salt.

[0031] The hardly soluble salt such as Li_2CO_3 is hardly dissolved in a solvent of the generally used organic electrolytic solution. When it forms the double salt with the organic metal salt, it can be dissolved in such solvent. In addition, the organic metal salt is further stabilized preferably.

[0032] The hardly soluble salt to be used is preferably hardly dissolved in an organic solvent which is used in the common cells. Specific examples of the hardly soluble salt are LiOH, Li_2CO_3, LiF, Li_2SO_4, Li_3PO_4, and the like. Among them, the alkali metal salts such as LiOH and Li_2CO_3 are preferred. In particular, Li_2CO_3 is preferred.

[0033] To calculate the molar ratio of the counter cation to the atom forming the anion center, the molar numbers of the cations and anions of the common electrolyte are not taken into account.

[0034] Examples of the organic solvent in which the above electrolyte is dissolved in the preparation of the electrolytic solution are ethers (e.g., 1,2-dimethoxyethane, 1,2-dimethoxymethane, dimethoxypropane, 1,3-dioxolane, tetrahydrofuran, 2-methyltetrahydrofuran, 4-methyl-1,3-dioxolane, etc.), esters (e.g., propylene carbonate, ethylene carbonate, butylene carbonate, γ-butyrolactone, γ-valerolactone, etc.), sulfolane, and the like.

[0035] Among them, the esters are preferred, since they have less reactivity with the metal salt on the positive electrode at a high voltage of 4.2 V or larger and will improve the shelf stability of the electrolytic solution, when they are used in combination with the electrolyte comprising the above organic metal salt. An amount of the ester in the organic solvent is preferably at least 10 % by volume, more preferably at least 20 % by volume, most preferably at least 30 % by volume.

[0036] A concentration of the electrolyte in the electrolytic solution is not critical. Usually, in the organic solvent, the electrolyte comprising the above organic metal slat is dissolved in a concentration of from 0.01 to 2 mol/liter, preferably from 0.05 to 1 mol/liter. In assembling the cell using the above described electrolytic solution, as a negative electrode, there is used an integral member of an alkali metal or a compound comprising the alkali metal and a collector material such as a stainless steel net.

[0037] Examples of the alkali metal are lithium, sodium, potassium, and examples of the compound comprising the alkali metal are alloys of the alkali metals with aluminum, lead, indium, cadmium, tin, magnesium, and the like; a compound of the alkali metal and carbon; and compounds of the lower potential alkali metals with metal oxides or sulfides (e.g. Nb_2O_6).

[0038] A positive electrode is produced by compounding a positive electrode active material such as a metal oxide (e.g., manganese dioxide, vanadium pentoxide, chromium oxide, lithium cobalt oxide, lithium nickel oxide, etc.) or a metal sulfide (e.g., molybdenum disulfide, etc.) and necessary additives such as a conductive aid or a binder (e.g., polytetrafluoroethylene, etc.), and molding it around a core of a current collector member such as a stainless steel net.

[0039] When the metal oxide is used as the positive electrode active material, a high voltage is generated. When the metal oxide which generates the voltage of at least 3 V, in particular at least 4.2 V is used in the positive electrode, the conventional cell comprising $LiBF_4$ or $LiB(C_6H_5)_4$ has decreased shelf stability. But, the electrolytic solution comprising the above organic metal salt to be used according to the present invention does not decrease the shelf stability of the cell at such high voltage. Therefore, the effects of the present invention is remarkably achieved, when the high voltage positive electrode active material is used. As a specific surface area of the positive electrode active material decreases, the shelf stability of the cell further increases. In the present invention, the positive electrode active material has preferably a surface area of 50 m /g or less, more preferably 30 m^3/g or less, especially 20 m^2/g or less.

[0040] Preferably, an active surface of the metal oxide of the active electrode active material is treated with a compound of an alkali metal or an alkaline earth metal, since the shelf stability is further improved. When the cell is predischarged after the assembly of the cell, the shelf stability of the cell is improved to some extent.

[0041] The present invention will be illustrated by the following Examples, which do not limit the scope of the present invention in any way. In Examples, "parts" are by weight.

Example 1

[0042] Using lithium boron disalicylate having the formula of $LiB(-O-C(=O)-C_6H_4-O-)_2$ (hereinafter referred to as "LiBSA") as an electrolyte, an electrolytic solution was prepared. In LiBSA, two electron attractive organic groups of the formula:- $C(=O)-C_6H_4-$ are bonded to the boron atom forming the anion center through the respective oxygen atoms. The molar ratio of the metal element (counter cation) to the atom forming the anion center was 1 .02.

[0043] First, LiBSA was dissolved in 1 ,2-dimethoxyethane (DME), and to the mixture, propylene carbonate (PC) was added and mixed to obtain an electrolytic solution. A volume ratio of propylene carbonate to 1 ,2-dimethoxyethane was 1:2, and a concentration of the LiBSA in the electrolytic solution was 0.6 mol/l. The composition of this electrolytic solution is expressed by "0.6 mol/l MBSA/PC:DME (volume ratio of 1:2)".

[0044] A mass of electrolytic manganese dioxide was heat treated and further treated with an aqueous solution of lithium hydroxide to obtain an active material having a specific surface area of 18 m/g. The manganese oxide active material (100 parts), carbon black (5 parts) and polytetrafluoroethylene powder (5 parts) were mixed, and the mixture was coated over both surfaces of a stainless steel net to form a sheet having a thickness of 0.4 mm and a width of 30 mm. After bonding a stainless steel net current collector to the sheet-form positive electrode, the electrode was dried at 250°C, and cooled down to room temperature in a dry atmosphere.

[0045] Then, the sheet-form positive electrode was sandwiched between a pair of microporous polypropylene films each having a thickness of 25 urn as separators. Over the sandwiched positive electrode, there was laminated a negative electrode comprising a sheet form lithium having a thickness of 0.18 mm and a width of 30 mm which was press bonded to a stainless steel net. Then, the laminated positive and negative electrodes were spirally wound to form a spiral electrode body, which was inserted in a cell case having a cylinder form with a bottom and an outer diameter of 1 5 mm.

[0046] After spot welding lead wires for the positive and negative electrodes, the above prepared electrolytic solution was filled in the cell case.

[0047] Thereafter, the opening of the cell case was sealed by a conventional method, and the cell was predischarged and aged at GOT for 3 days to produce an organic electrolytic solution cell having a structure of the Figure.

[0048] The cell of the Figure comprises a positive electrode 1, a negative electrode 2, a separator 3 and an electrolytic solution 4. For simplicity, the stainless steel nets used in the production of the positive and negative electrodes 1 and 2, and current collectors are not shown.

[0049] The cell further comprises a cell case 5 made of stainless steel, and the cell case 5 functions also as a negative electrode terminal. At the bottom of the cell case, an insulator 6 made of a polytetrafluoroethylene sheet is provided. On the inner peripheral wall surface of the cell case, an insulator 7 made of a polytetrafluoroethylene sheet is provided. The spiral electrode body consisting of the positive and negative electrode 1, 2 and the separator 3, and the electrolytic solution 4 are contained in the cell once 5.

[0050] The opening of the cell case 5 is closed with a sealing plate 8 made of stainless steel. The sealing plate has a gas vent hole 8a at its center. The sealing section has an annular packing 9 made of polypropylene, a flexible thin plate 10 made of titanium, and a thermally deformable annular member 11 made of polypropylene.

[0051] Since the thermally deformable member 11 is deformed by the temperature change, it changes a breaking pressure of the flexible plate 10.

[0052] The cell further comprises a terminal plate made of rolled steel plate 12 plated by nickel. The plate 12 has a cutting edge 12a and a gas vent hole 12b. When a gas is generated in the cell and the internal pressure increases, the flexible thin plate 10 is deformed by the increased internal pressure and broken by the cutting edge 12a, then the gas in the cell is exhausted through the hole 12b, whereby the breakage of the cell is prevented.

[0053] The cell has an insulating packing 13 and a lead member 14. The lead member 14 electrically connects the positive electrode 1 and the sealing plate 8, and the terminal plate 12 functions as the positive electrode terminal since it contacts to the sealing plate 8, and the terminal plate 12 functions as the positive electrode terminal since it contacts to the sealing plate 8. A lead member 15 electrically connects the negative electrode 2 and the cell case 5.

COMPARATIVE EXAMPLE 1

[0054] In a mixed solvent of PC and DME in a volume ratio of 1 : 2, $LiB(C_6H_5)_4$ • 3DME was dissolved to obtain an electrolytic solution having a composition of "0.6 mol/l $LiB(C_6H_5)_4$/PC:DME (1:2)". The molar ratio of the metal element (counter cation) to the atom forming the anion center of $LiB(C_6H_5)_4$ • 3DME was 1.00.

[0055] In the same manner as in Example 1 except that this electrolytic solution was used, a cylindrical organic electrolytic solution cell having the structure of the Figure was assembled.

COMPARATIVE EXAMPLE 2

[0056] In a mixed solvent of PC and DME in a volume ratio of 1:2, $LiBF_4$ was dissolved to obtain an electrolytic solution having a composition of "0.6 mol/l $LiBF_4$/PC:DME (1:2)". The molar ratio of the metal element (counter cation) to the atom forming the anion center of $LiBF_4$ was 1.00.

[0057] In the same manner as in Example 1 except that this electrolytic solution was used, a cylindrical organic electrolytic solution cell having the structure of the Figure was assembled.

[0058] With each of the cells assembled in Example 1 and Comparative Examples 1 and 2, a minimum voltage was measured when the cell was discharged at 3 A for 0.5 second. Each cell was stored at 80 °C for 10 days, and the minimum voltage was measured in the same manner as above and compared with the original minimum voltage before storing to check the degradation of the property of each cell. The results are shown in Table 1.

[0059] Separately, each of another set of cells was charged at 100 mA up to 3.5 V, and the minimum voltage was measured when each cell was discharged at 0.3 A for 10 msec. Then, the cell was stored under the constant voltage condition of 3.5 V at 80 °C for 10 days, and thereafter the minimum voltage was measured under the same conditions as above to determine the deterioration of the cell property. The results are also shown in Table 2.

Table 1

Example No.	Minimum voltage (V) after discharge at 3 A for 0.5 sec.	
	Before storage	After storage
Ex.1	1.37	1.06
Comp. 1	1.06	0.02
Comp. 2	1.30	<0.00

Table 2

Example No.	Minimum voltage (V) after discharge at 3 A for 10 msec.	
	Before storage	After storage
Ex.1	3.07	2.93
Comp. 1	*1)	---
Comp. 2	3.10	0.94

Note *1) The cell could not be charged up to 3.5 V.

[0060] As seen from the results of Table 1, after the storage under the severe conditions of 80 °C for 10 Days, the minimum voltage of the cell of Example 1 decreased from 1.37 V to 1.06 V, but this decrease of the minimum voltage was much smaller than that found in the cells of Comparative Examples 1 and 2.

[0061] That is, with the cell of Comparative Example 1 using $LiB(C_6H_5)_4$ as the electrolyte, the minimum voltage decreased from 1.06 V to 0.02 V, and with the cell of Comparative Example 2 using $LiBF_4$ as the electrolyte, the minimum voltage decreased from 1.30 V to 0.00 V. These comparative cells cannot be used practically.

[0062] As seen from the results of Table 2 the cell of Example 1 using the electrolyte in which the electron attractive group is bonded to the anion center atom through the oxygen atom showed the small decrease of voltage even at a high voltage of 3.5 V or higher and had good shelf stability in comparison with the cell of Comparative Example 2 using the electrolyte having the electron attractive group which is not bonded to the anion center atom through the oxygen atom. The cell of Comparative Example 1 which used the electrolyte having no electron attractive group could not be charged up to 3.5 V since the electrolyte was decomposed before the voltage reached 3.5 V.

[0063] These results show that the cell of the present invention has much better shelf stability than the conventional cells.

Claims

1. An organic electrolytic solution cell having a cell voltage exceeding 3 V comprising a positive electrode, a negative electrode which is made of an alkali metal or a compound comprising an alkali metal, and an organic electrolytic solution which contains, as an electrolyte, an organic salt comprising an anion having an atom selected from the elements of the IIIb, IVb and Vb groups of the Periodic Table as an anion center in which an electron attractive group is bonded to said atom, and a counter cation in a molar ratio of said counter cation to said anion center atom of larger than 1.

2. The organic electrolytic solution cell according to claim 1, wherein said molar ratio is at least 1.005.

3. The organic electrolytic solution cell according to claim 1, wherein said molar ratio is not larger than 1.05.

Patentansprüche

1. Zelle mit organischer Elektrolytlösung, die eine Zellspannung von über 3 V aufweist, umfassend eine positive Elektrode, eine negative Elektrode, die aus einem Alkalimetall oder einer ein Alkalimetall umfassenden Verbindung besteht, und eine organische Elektrolytlösung, die als Elektrolyt ein organisches Salz enthält, das ein Anion mit einem Atom, das aus den Elementen der Gruppen IIIb, IVb und Vb des Periodensystems ausgewählt ist, als Anionzentrum, wobei eine elektronenziehende Gruppe an das Atom gebunden ist, und ein Gegenkation in einem Stoffmengenverhältnis des Gegenkations zu dem Atom des Anionzentrums von mehr als 1 umfasst.

2. Zelle mit organischer Elektrolytlösung gemäß Anspruch 1, wobei das Stoffmengenverhältnis wenigstens 1,005 beträgt.

3. Zelle mit organischer Elektrolytlösung gemäß Anspruch 1, wobei das Stoffmengenverhältnis nicht größer als 1,05 ist.

Revendications

1. Pile à solution électrolytique organique possédant une tension de pile qui dépasse 3 V, comprenant une électrode

positive, une électrode négative qui est faite d'un métal alcalin ou d'un composé comprenant un métal alcalin, et une solution électrolytique organique qui contient, en tant qu'électrolyte, un sel organique comprenant un anion qui possède un atome choisi parmi les éléments des groupes IIIb, IVb et Vb du tableau périodique comme centre anionique où un groupement attracteur d'électrons est lié audit atome et un contre-cation qui est dans un rapport plus grand que 1 avec ledit atome du centre anionique.

2. Pile à solution électrolytique organique selon la revendication 1, où le rapport molaire est d'au moins 1,005.

3. Pile à solution électrolytique organique selon la revendication 1, où le rapport molaire n'est pas supérieur à 1,05.

Figure

